1,013,441

PATENT SPECIFICATION

NO DRAWINGS

1,013,441

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Int. Cl.:— C 07 c, d // A 01 n, C 11 b

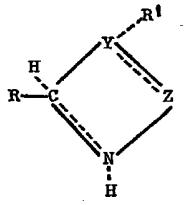
COMPLETE SPECIFICATION

Novel 2,6-Dihalophenyl Heterocyclic Compounds and Compositions containing them

We, "SHELL" RESEARCH LIMITED, a British Company of Shell Centre, London, S.E.1, (formerly of St. Helen's Court, Great St. Helen's, London, E.C.3), do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the novel heterocyclic compounds hereinafter specified. These compounds have herbicidal properties, being especially toxic to germinating seeds. Accordingly, this invention also relates to herbicidal compositions containing said novel compounds and to a method for eradicating weeds from crop areas bearing, or intended to bear crops, which comprises applying to said areas a compound or composition of the invention. Some of the compounds also posses pharmacological properties, especially general metabolic depressant properties, and others fungicidal and/or bacteriostatic properties.

The novel compounds of the invention have the general formula



wherein the carbon and nitrogen atoms are linked either by a double bond or by a single bond and the remaining valencies of said atoms attached to hydrogen atoms;

R represents a 2,6-dihalophenyl group; preferably a 2,6-dichlorophenyl group;

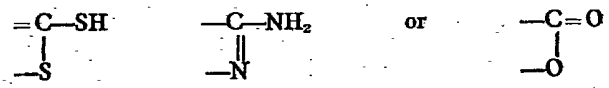
Y represents an oxygen, sulphur or nitrogen atom, the third valency of said nitrogen atom being attached either to Z to form a double bond therewith, or to R^1, R^1 representing a hydrogen atom or a phenyl group;

Z represents an organic group which, with the atoms to which it is linked, completes a heterocyclic ring; and the acid addition salts thereof. The acid addition salts of said compounds are formed with organic or inorganic acids, for example hydrohalic acids, particularly hydrochloric and hydrobromic acids, sulphuric, nitric, phosphoric, acetic, glycollic, lactic, succinic, citric, salicylic, ethane sulphonic or hydroxyethane sulphonic acid.

Z preferably represents an alkylene, alkyleneoxy, alkylenecarbonyl or alkenylene group containing up to 4 carbon atoms which group may contain alkyl, haloalkyl, chlorophenoxyalkyl, phenyl, halophenyl or alkoxycarbonyl, substituents, or a phenylene or tetrahydrophenylene group, or one of the following groups:—

[Pri

Pric



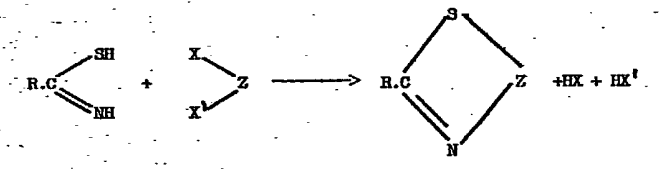
Where Z contains alkyl or haloalkyl substituents, these substituents preferably contain 1 to 4 carbon atoms. Chloro- or bromo-alkyl or chloro- or bromo-phenyl groups are the preferred haloalkyl or halophenyl substituents. As mentioned above, the compounds of the invention form acid addition salts and those which are particularly preferred are those of hydrochloric and hydrobromic acid.

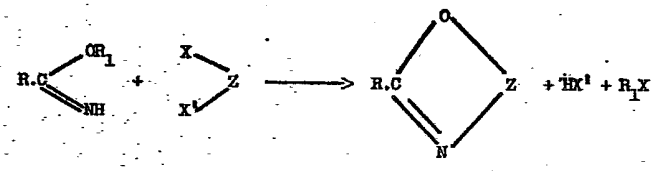
The novel compounds of the invention may exist in tautomeric forms and these are included within the scope of the invention.

The novel compounds of the invention may be prepared by methods known for the preparation of heterocyclic compounds.

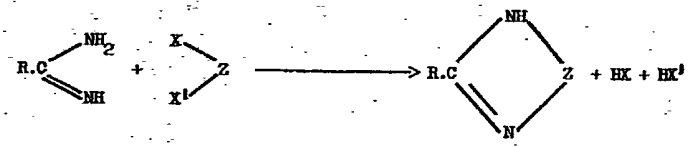
A method for the preparation of compounds of the above general formula wherein Z represents a substituted or unsubstituted alkylene or alkyleneoxy group comprises reacting at an elevated temperature a 2,6-dihalothiobenzamide, a 2,6-dihalobenzimidic ester, a 2,6-dihalobenzamidine, or a 2,6-dihalobenzamidoxime, with a compound of formula XZX^1 wherein X and Z^1 each represent a halogen atom or a sulphuric ester group and Z has the above meaning.

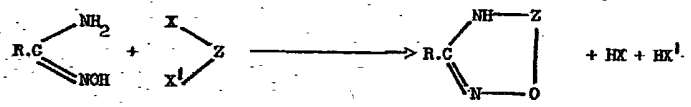
The respective reactions involved may be represented by the following equations:—





(R_1 represents a hydrocarbyl group preferably an alkyl group, forming a readily volatile halide R_1X, for example, methyl or ethyl)

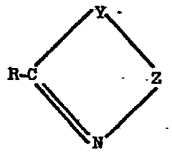
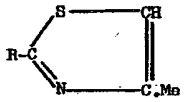
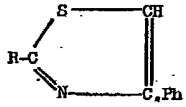
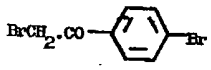
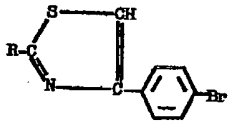
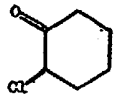
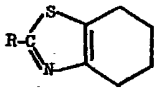
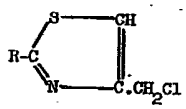




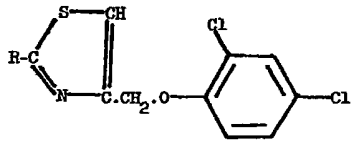
The reactants are heated together for several hours, the actual temperatures and period of heating depending on the particular reactants employed. In general, reaction temperatures in the range 50° to 150°C., preferably about 100°C. and periods of 2 to 24 hours may be used. The reaction may be effected in an inert solvent, for example, an alcohol such as ethyl alcohol or glycol, an ethereal solvent such as dimethoxyethane, dioxane or tetrahydrofuran, a ketonic solvent such as acetone, or a hydrocarbon solvent such as benzene or toluene. The reaction may be effected in presence or absence of a hydrogen halide acceptor, for example, a tertiary nitrogenous base such as pyridine or

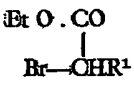
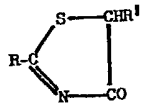
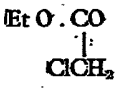
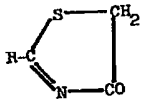
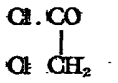
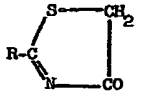
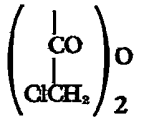
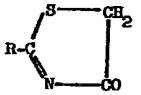
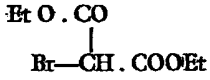
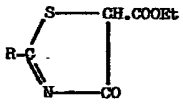
triethylamine. Anhydrous or substantially anhydrous conditions are preferably employed. The desired reaction product may be produced in the form of its hydrohalide. This can readily be converted to the free base by treatment with an alkali or alkaline reacting salt, for example sodium bicarbonate or sodium acetate.

A method for the preparation of compounds having the above general formula wherein Z represents an alkenylene group may be prepared by reacting a 2,6-dihalobenzimidic ester, 2,6-dihalothiobenzamide or 2,6-dihalobenzamidine with a compound containing an α-halo-carbonyl group, for example, an α-haloketone or an α-halocarboxylic acid, ester, acid halide or acid anhydride, particularly with the α-chloro- or α-bromo-carbonyl compounds. The reaction may be carried out by heating the reactants together in absence of a solvent or in the presence of an inert solvent, for example a hydrocarbon solvent, preferably an aromatic hydrocarbon solvent such as toluene or a halogenated hydrocarbon solvent. Water produced in the reaction is preferably removed, for example, azeotropically. Reaction temperatures in the range 70° to 120°C. are in general satisfactory but higher or lower temperatures may be used if desired. Examples of compounds which may be made by this process from 2,6-dichlorothiobenzamide and the α-halocarbonyl compound stated are given below. Analogous products are obtained from the 2,6-dichlorobenzimidic ester or amidine.

α-Halocarbonyl compound	Product 
A) *α-Haloketone* $ClCH_2 . CO . CH_3$	
$ClCH_2 . CO . Ph$	
	
	
$ClCH_2 . CO . CH_2Cl$	

The chlorine atom in the last compound is active and can be reacted with salts of carboxylic acids, for example, alkali metal or silver salts thereof, to produce the corresponding esters, or with alkali or alkaline earth metal phenoxides to produce the corresponding phenyl ethers, for example the compound



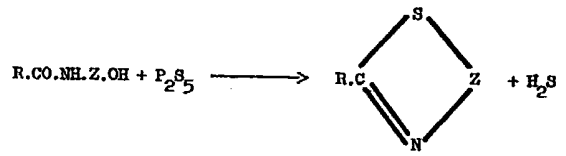
B) *α-Halocarboxylic ester; chloride or anhydride*	*Product*	
		or a tautomer thereof
(R¹ = Me, Et, *n*-Pr, *n*-Bu)		
		or a tautomer thereof
		or a tautomer thereof
		or a tautomer thereof
		

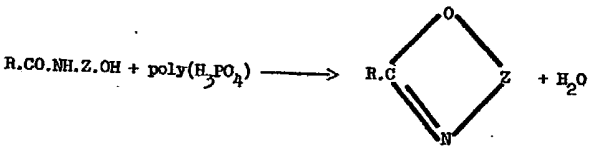
The heterocyclic compound is in general produced in the form of a hydrohalide which is readily converted to the free base by treatment with alkali.

Compounds of the above general formula in which Y represents a sulphur or an oxygen atom may be prepared by cyclising a 2,6-dihalobenzamide derivative of formula

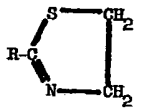
R . CO . NH . Z . OH

wherein R and Z have the aforesaid meanings, by treatment respectively with phosphorus pentasulphide, or with phosphorus pentoxide, polyphosphoric acid or other compound capable of extracting the elements of water from the benzamide derivative. The reactions may be represented by the following equations:—





The group represented by Z should not contain any atoms or groups which will be affected under the reaction conditions. The reaction is effected by heating the reactants together, preferably in an inert solvent, for example, a hydrocarbon solvent such as toluene. Temperatures in the range 80°—150°C. are suitable. In this way were prepared, for example, 2-(2,6-dichlorophenyl)-1,3-thiazoline,

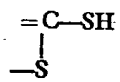


and the 4-methyl, 5-ethyl, 4,4-dimethyl and 4,5-dimethyl derivatives.

Compounds of the invention in which Z represents a methyleneoxy or carbonyloxy group and Y represents —N— or —NH— i.e. oxadiazole derivatives, may be prepared by cyclising an ester, or O-alkoxycarbonyl derivative, of 2,6-dihalo-α-aminobenzaldoxime at a temperature sufficient to effect cyclisation. The reaction may be represented as follows:—

wherein R° represents an alkyl or haloalkyl group. Temperatures in the range 140°—180°C. are suitable to effect cyclisation of these oxime esters, but higher or lower temperatures may be employed. When water or the appropriate alcohol is no longer produced, the reaction is generally complete and heating may be stopped. Cyclisation may be effected in the presence of an inert solvent, but a solvent is in general unnecessary.

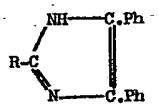
Compounds of the invention in which Z represents the group



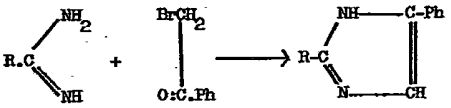
and Y is N, i.e. thiadiazole derivatives may be prepared by condensing a 2,6-dihalobenzamidoxime with carbon disulphide at an elevated temperature. The reaction is

preferably carried out in an aqueous methanol medium. After removing the solvents, the residue is then treated with concentrated hydrochloric acid which causes a vigorous evolution of gas. Water is then added, the mixture heated to boiling and the acid solution removed. The desired compound is extracted from the residue with aqueous alkali metal hydroxide and re-precipitated by the addition of mineral acid.

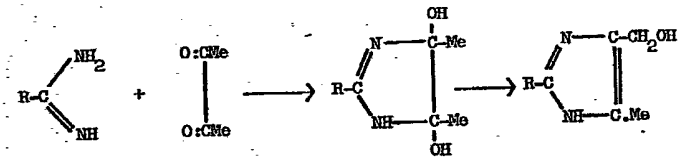
Compounds of the invention in which the heterocyclic ring is an imidazole or substituted imidazole ring can be prepared by adapting methods normally applied to the preparation of this type of heterocyclic ring. Thus, 2,6-dihalobenzaldehyde may be condensed with a compound containing vicinal carbonyl groups, particularly benzil and its derivatives, in the presence of ammonia. The reactants are heated together, if necessary in presence of an inert solvent. Dry ammonia gas may be passed continuously through the reaction mixture. Instead of ammonia, an ammonium salt which dissociates under the reaction conditions may be used, for example, ammonium acetate. The reaction may be carried out at atmospheric or superatmospheric pressure. For example, the compound made in this way from 2,6-dichlorobenzaldehyde and benzil has the structure



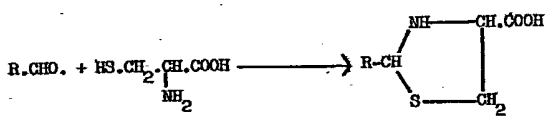
Alternatively, a 2,6-dichlorobenzamidine may be condensed with an α-halogeno- or α-hydroxyketone. The reaction with ω-bromoacetophenone, for example, can be represented by the following equation:—



2,6-Dihalobenzamidines may also be condensed with α-dicarbonyl compounds. The reaction with diacetyl, for example may be represented by the following equation:—

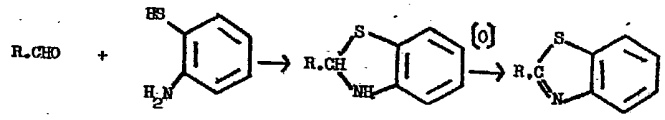


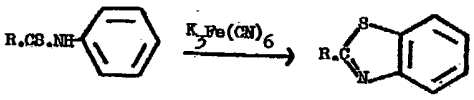
Tetrahydrothiazole derivatives may be prepared by condensing a 2,6-dihalobenzaldehyde R.CHO with an aliphatic β-aminothiol. The reaction with 1-amino-2-mercaptopropionic acid, for example, may be represented by the following equation:—



Oxidation of the product, for example with alkaline potassium ferricyanide fails to yield the desired dihydrothiazole, but results instead in regeneration of the aldehyde.

By condensing a 2,6-dihalobenzaldehyde R . CHO with 2-aminothiophenol, suitably in presence of a base, preferably a tertiary nitrogenous base such as pyridine, 2-(2,6-dihalophenyl)-2,3-dihydrobenzthiazole is obtained. This compound can be oxidised with alkaline potassium ferricyanide solution to 2-(2,6-dichlorophenyl)benzthiazole. This product is also obtained by oxidising N-phenyl-2,6-dichlorothiobenzamide with alkaline potassium ferricyanide solution. These reactions may be represented by the following equations:—

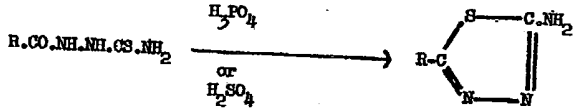




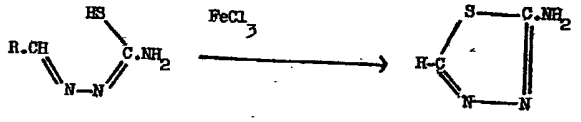
2-(2.6-Dihalophenyl)-1,2-dihydrobenzimidazole may be similarly prepared by condensing a 2,6-dihalobenzaldehyde with *o*-phenylenediamine in an inert solvent, for example, benzene, preferably with simultaneous removal of the reaction water. While it does not appear possible to oxidise this product with, for example, alkaline potassium ferricyanide, to the benzimidazole, the benzimidazole can be prepared in one step by reacting the aldehyde and the diamine in presence of cupric acetate when condensation and oxidation occur simultaneously to give 2-(2,6-dihalophenyl)benzimidazole. These benzimidazoles are suitably isolated as their salts, preferably the hydrochlorides.

2-(2,6-Dihalophenyl)-2,3-dihydrobenzoxazole can be similarly prepared by condensing the aldehyde R . CHO with 2-aminophenol but attempted oxidation of this product gave only the aldehyde R . CHO. The infra-red spectrum of the benzoxazole showed that no hydroxyl group was present.

Thiadiazole derivatives according to the invention may be prepared by cyclising 2,6-dihalobenzoyl thiosemicarbazide R . CO . NH . NH . CS . NH_2 by treatment with a substance capable of removing the elements of water from its molecule, for example, sulphuric or phosphoric acid. The reaction may be represented by the equation:—

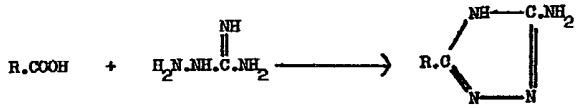


The same product can be obtained by treating the thiosemicarbazone of 2,6-dihalobenzaldehyde with a mild oxidising agent, for example, ferric chloride. The reaction can be represented thus:—

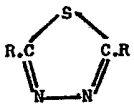


The reaction is preferably effected at an elevated temperature, suitably at 90° to 100°C. It is suitably effected in an aqueous medium.

Triazole derivatives may be prepared by condensing a 2,6-dihalobenzoic acid R . COOH with guanidine or a substituted guanidine, for example, amino-guanidine or nitroguanidine. The reaction with aminoguanidine can be represented thus:—



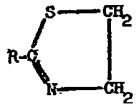
2,6-dihalobenzalazine R . CH=N—N=CH . R on treatment with phosphorus pentasulphide gives the product:



The following Examples illustrate the novel compounds of the invention and their preparation. In these Examples, parts by weight (w) and parts by volume (v) bear the same relation as the kilogram and the litre, and, in the formulae the symbol R represents the 2,6-dichlorophenyl group.

EXAMPLE I.

Preparation of 2-(2,6-dichlorophenyl)-1,3-thiazoline



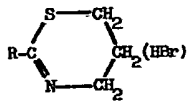
2,6-Dichlorothiobenzamide (10 w) and ethylene dibromide (10 v) were heated together on a boiling water bath for 6 hours. The cooled product was washed three times with 50 v of hexane and three times by boiling with benzene (50 v). The pale brown somewhat sticky insoluble residue was boiled four times with ethanol (50 v). The alcohol extract was evaporated to small bulk and water added until cloudy. Crystals separated on cooling. These were recrystallised from aqueous methanol to give white prisms (2 v), m.p. 73°C.

Analysis

Found: N 6.0, Cl 30.5, S 13.6;
$C_9H_7Cl_2NS$ requires: N 6.0, Cl 30.6, S 13.8%

EXAMPLE II.

Preparation of 2-(2,6-dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine and its hydrobromide



A mixture of 2,6-dichlorothiobenzamide (50 w), 1,3-dibromopropane (50 v) and 1,2-dimethoxyethane (250 v) was heated at reflux temperature for 18 hours, the solid which separated being periodically removed by filtration. The combined solids were washed well with ether and air dried to give a white powder (60 w) melting at 196° to 198°C. with decomposition.

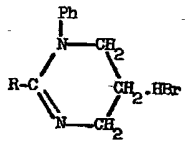
Analysis

Found: C 34.1, H 2.5, N 4.3, S 11.6, Br 24.2%
$C_{10}H_{10}BrCl_2NS$ requires: C 36.5, H 3.1, N 4.3, S 9.8, Br 24.4%

The compound was shaken with water (50 v) and filtered. The clear solution was treated with a slight excess of aqueous sodium bicarbonate solution and the thiazine thereby precipitated was collected and air-dried. Crystallisation from light petroleum (b.p. 80° to 100°C.) gave white plates, melting at 104° to 105°C. The mixed melting point with the product obtained in Example XXI showed that the products were identical.

EXAMPLE III.

Preparation of 1-phenyl-2-(2,6-dichlorophenyl-1',4,5,6-tetrahydropyrimidine hydrobromide



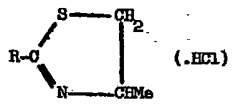
N-Phenyl-2,6-dichlorobenzamidine (1.5 w) and 1,3-dibromopropane (0.7 w) in dimethoxyethane (20 v) were refluxed for 13 hours, then cooled and diluted with ether. A solid crystallised from the solution (1.0 w), m.p. 255° to 258°C.

Analysis

Found: C 49.9, H 4.1, N 7.2, Cl 18.3, Br⁻ 20.7%
$C_{16}H_{15}BrCl_2N_2$ requires: C 49.8, H 3.9, N 7.8, Cl 18.4, Br⁻ 20.7%

EXAMPLE IV.

Preparation of 2-(2,6-dichlorophenyl)-4-methyl-1,3-thiazoline and its hydrochloride



2,6-dichlorothiobenzamide (20 w) and 1,2-dibromopropane (50 v) were heated together under reflux for 8 hours and then cooled. The semi-solid mass so obtained was triturated with ether until brown colour was no longer eluted. The grey residue (25 w) was shaken with 2 N-hydrochloric acid (500 v) and filtered from tar. The filtrate was neutralised with sodium bicarbonate and then extracted with ether. The ether extract was dried over anhydrous magnesium sulphate, the ether removed and the residue distilled, the thiazoline being obtained as a yellow oil b.p. 113-114°C. at 1.5 mm pressure.

Analysis

Found: C 49.2, H 3.9, C 6.0, Cl 29.4, S 13.0%
$C_{10}H_9Cl_2NS$ requires: C 48.8, H 3.7, N 5.7, Cl 28.9, S 13.0%

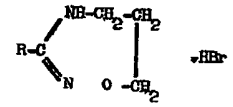
The hydrochloride was prepared by dissolving the thiazoline (10 w) in ether (500 v) and then saturating the solution with hydrogen chloride. The white precipitate was filtered off, washed with ether and air-dried. It had m.p. 205° to 206°C. with decomposition.

Analysis

Found: C 42.1, H 3.3, N 4.8, Cl 37.3, S 11.7, Cl⁻ 12.7%
$C_{10}H_{10}NSCl_3$ requires: C 42.5, H 3.5, N 5.0, Cl 37.7, S 11.3, Cl⁻ 12.6%

EXAMPLE V.

Preparation of 3-(2,6-dichlorophenyl)-4,5,6,7-tetrahydro-1,2,4-oxadiazepine hydrobromide



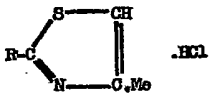
2,6-Dichlorobenzamidoxime (2.05 w) and 1,3-dibromopropane (2.02 w) in dimethoxyethane (50 v) were refluxed for 3 hours. The product was precipitated by adding ether to the cooled reaction mixture and was then filtered off and washed well with acetone. It had m.p. 228° to 230°C. Yield 2 w.

Analysis

Found: C 36.8, H 3.3, N 8.6, Cl 22.1, Br 24.2%
$C_{10}H_{11}BrCl_2N_2O$ requires: C 36.8, H 3.4, N 8.6, Cl 21.8, Br 24.4%

EXAMPLE VI.

Preparation of 4-methyl-2-(2,6-dichlorophenyl)-1,3-thiazole hydrochloride



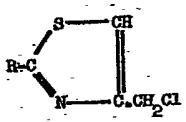
A mixture of 2,6-dichlorothiobenzamide (20 w) and chloracetone (10 w) was refluxed in benzene (350 v) for 18 hours under a Dean and Stark head. Hydrogen chloride was evolved and water was collected. Benzene was stripped off and the residue was extracted six times with 200 v of light petroleum (b.p. 60° to 80°C.). The insoluble tarry matter was rejected. The solution was evaporated to small bulk and cooled whereon a small amount (0.8 w) of 2,6-dichlorothiobenzamide separated and was removed. The remaining solution was freed from solvent and the residue distilled, an oil boiling at 117°C. under 0.5 mm and containing some suspended solid being obtained. The distillate was dissolved in ether and treated with dry hydrogen chloride, a white powder (10 w) being obtained which melted at 175°C. with shrinkage from 169°C.

Analysis

Found: C 42.8, H 2.7, N 5.3, Cl 38.2%
$C_{10}H_6Cl_3NS$ requires: C 42.6, H 2.8, N 5.0, Cl 38.0%

EXAMPLE VII.

Preparation of 4-chloromethyl-2-(2,6-dichlorophenyl)-1,3-thiazole



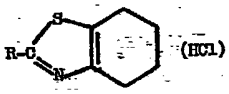
2,6-Dichlorothiobenzamide (34 w) and 1,3-dichloropropane-2-one (25 w) in 1,2-dimethoxyethane (250 v) were refluxed for 24 hours. The solvent was then stripped off under reduced pressure leaving a brown oily residue which was dissolved in ether and filtered. The filtrate was saturated with dry hydrogen chloride. The resulting precipitate was filtered off, shaken with ether (500 v) and water and the aqueous layer separated. The ethereal layer was washed twice with water (250 v) dried over anhydrous magnesium sulphate and the ether distilled from the mixture. The residue was distilled under reduced pressure giving a colourless liquid, b.p. 149°C. under 0.3 mm. pressure.

Analysis

Found: C 42.9, H 2.3, S 11.3%
$C_{10}H_6Cl_3NS$ requires: C 43.1, H 2.1, S 11.5%

EXAMPLE VIII.

Preparation of 2-(2,6-dichlorophenyl)-4,5,6,7-tetrahydrobenzthiazole and its hydrochloride



2,6-Dichlorothiobenzamide (20 w) and 2-chlorocyclohexanone (30 w) were heated together at 120°C. A yellow solution formed at first from which solid gradually separated. After 4 hours, the mixture was cooled and extracted twice with ether (250 v)—solution A. The residual off-white solid (20 w) was dissolved in methanol (200 v), treated with decolourising charcoal and diluted with ether (500 v). From the clear

solution, the thiazole hydrochloride separated as colourless prisms (18 w) m.p. 190°C. with decomposition. A further quantity (8.5 w) was obtained by saturating solution A with hydrogen chloride and washing the precipitate with ether.

Analysis

Found: C 48.9, H 3.9, N 4.3, Cl 33.2, S 10.3, Cl⁻ 10.7%;
$C_{13}H_{11}Cl_3NS$ requires C 48.6, H 3.7, N 4.4, Cl 33.4, S 10.0, Cl⁻ 11.1%

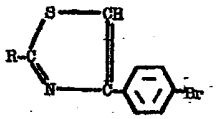
The free base was prepared by hydrolysing the hydrochloride with water, or aqueous sodium acetate or aqueous sodium bicarbonate. The base was extracted from the mixture with ether, the ethereal extract dried, the ether removed and the residue crystallised from light petroleum (b.p. 60° to 80°C.) giving stout prisms m.p. 95°C.

Analysis

Found: C 55.1, H 4.0, N 4.8, Cl 25.2, S 11.6%;
$C_{15}H_{11}Cl_2NS$ requires: C 55.0, H 3.9, N 4.9, Cl 25.0, S 11.3%

EXAMPLE IX.

Preparation of 4-(4-bromophenyl)-2-(2,6-dichlorophenyl)-1,3-thiazole



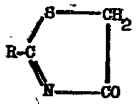
2,6-Dichlorothiobenzamide (20 w) and 4-bromophenacyl bromide (25 w) in 1,2-dimethoxyethane (300 v) were refluxed for 20 hours and the solvent then stripped off. The residue was dissolved in hot ethanol and treated with decolourising charcoal. On cooling, colourless prisms separated which were collected and air-dried. The thiazole (13.3 w) had m.p. 166°C., unchanged by recrystallisation from light petroleum (b.p. 60° to 80°C.).

Analysis

Found: N 3.5, Cl 18.8, Br 20.9, S 8.7%;
$C_{15}H_{10}BrCl_2NS$ requires: N 3.6, Cl 18.4, Br 20.8, S 8.3%

EXAMPLE X.

Preparation of 2-(2,6-dichlorophenyl)-1,3-thiazol-2-in-4-one



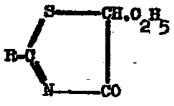
2,6-Dichlorothiobenzamide (50 w) and ethyl chloroacetate (33 w) were heated together on a steam bath until a homogeneous solution was obtained. Ethanol and hydrogen chloride were then removed from the mixture under reduced pressure. The residual solid was triturated with boiling ether and crystallised from methanol. The thiazolone formed colourless prisms (15 w), m.p. 212°C.

Analysis

Found: C 44.0, H 1.9, N 5.6, Cl 28.8, S 12.9%;
$C_9H_5NSOCl_2$ requires: C 43.9, H 2.0, N 5.7, Cl 28.8, S 13.0%

EXAMPLE XI.

Preparation of 5-ethyl-2-(2,6-dichlorophenyl)-1,3-thiazolin-4-one



2,6-Dichlorothiobenzamide (20 w) and ethyl 2-bromobutyrate (25 w) were heated together on a boiling water bath. The solid slowly dissolved and then solidification commenced. After 2 hours benzene (200 v) was added, the mixture was refluxed for 2 hours and then filtered hot. The residual solid was washed with hot benzene to give

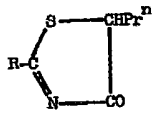
a white powder (25 w) m.p. about 215°C. Crystallisation from methanol gave colourless prisms m.p. 232°C.

Analysis

Found:	C 48.0,	H 3.3,	N 5.3,	Cl 25.8,	S 11.8%
$C_{11}H_9Cl_2NOS$ requires:	C 48.2,	H 3.3,	N 5.1,	Cl 25.9,	S 11.7%

EXAMPLE XII.

Preparation of 2-(2,6-dichlorophenyl)-5-n-propyl-1,3-thiazol-2-in-4-one



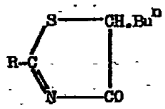
2,6-Dichlorothiobenzamide (20 w) and ethyl 2-bromovalerate (30 w) were heated together at 100°C. for 4 hours. The initial solution became semi-solid and, after cooling, the mixture was triturated with cold ether. The residue was crystallised from methanol giving pale lemon yellow crystals (10.5 w) m.p. 205° to 207°C.

Analysis

Found:	C 50.4,	H 3.6,	N 4.6,	Cl 24.9,	S 11.1%
$C_{12}H_{11}Cl_2NOS$ requires:	C 50.0,	H 3.8,	N 4.9,	Cl 24.7,	S 11.1%

EXAMPLE XIII.

Preparation of 5-n-butyl-2-(2,6-dichlorophenyl)-1,3-thiazol-2-in-4-one



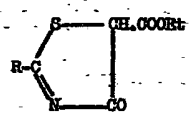
2,6-Dichlorothiobenzamide (20 w) and ethyl 2-bromocaproate (30 w) were heated together for 6 hours at 100°C. The resulting solution became semi-solid on cooling. The mixture was dissolved in the minimum of hot methanol. The crystals which separated on cooling were recrystallised from methanol to give white needles (5.5 w), m.p. 165°C.

Analysis

Found:	C 51.7,	H 4.0,	N 4.5,	Cl 23.6,	S 10.9%
$C_{13}H_{13}Cl_2NOS$ requires:	C 51.6,	H 4.3,	N 4.6,	Cl 23.5,	S 10.6%

EXAMPLE XIV.

Preparation of 2-(2,6-dichlorophenyl)-5-ethoxycarbonyl 1,3-thiazolin-4-one

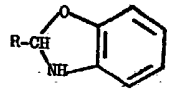


2,6-Dichlorothiobenzamide (10.3 w), diethyl bromomalonate (12.0 w) and methanol (200 v) were refluxed together for 8 hours. The solvent was then removed and the residue crystallised from methanol. The product (6.0 w) had m.p. 110° to 113°C.

Analysis

Found:	C 45.1,	H 3.0,	N 4.4,	Cl 22.8,	S 10.2%
$C_{12}H_9Cl_2NO_2S$ requires:	C 45.3,	H 2.8,	N 4.4,	Cl 22.3,	S 10.1%

EXAMPLE XV.
Preparation of 2-(2,6-dichlorophenyl)-2,3-dihydrobenzoxazole

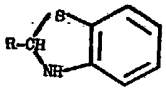


2,6-Dichlorobenzaldehyde (7 w) and *o*-aminophenol (4.4 w) in benzene (100 v) were refluxed under a Dean and Stark head until no further water was produced. The mixture was then evaporated to dryness and crystallised from light petroleum (b.p. 80° to 100°C.). The product had m.p. 79° to 81°C. Yield 7 w.

Analysis

Found:	C 58.8,	H 3.4,	N 5.6,	Cl 26.7%
$C_{13}H_9Cl_2ON$ requires:	C 58.7,	H 3.4,	N 5.3,	Cl 26.7%

EXAMPLE XVI.
Preparation of 2-(2,6-dichlorophenyl)-2,3-dihydrobenzothiazole

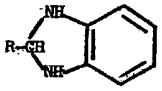


2-Aminothiophenol (6.3 w) and concentrated hydrochloric acid (5.0 v) were dissolved in pyridine (20 v) and the solution added to 2,6-dichlorobenzaldehyde (8.75 w) in pyridine (20 v). The mixture was shaken for 30 minutes, then heated in a boiling water bath for 30 minutes, cooled and poured on to a mixture of ice and hydrochloric acid. The sticky solid thus obtained was extracted with light petroleum (b.p. 60 to 80°C.), the extract dried and cooled. The crystalline solid which separated (2.5 w) had m.p. 94° to 96°C.

Analysis

Found:	C 55.7,	H 2.8,	N 5.0,	Cl 25.5,	S 11.4%
$C_{13}H_9Cl_2NS$ requires:	C 55.3,	H 3.2,	N 5.0,	Cl 25.2,	S 11.3%

EXAMPLE XVII.
Preparation of 2-(2,6-dichlorophenyl) benzamidazoline

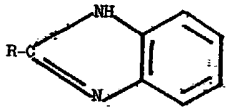


2,6-Dichlorobenzaldehyde (7.0 w), and *o*-phenylene-diamine (4.3 w) in benzene (100 v) were refluxed under a Dean and Stark head until all water had been removed. The benzene was then removed by distillation and the residue crystallised from light petroleum (b.p. 60° to 80°C.) when 9.0 w of product of m.p. 109° to 111°C. were obtained.

Analysis

Found:	C 58.8,	H 3.3,	N 10.6,	Cl 27.7%
$C_{13}H_{10}Cl_2N_2$ requires:	C 59.0,	H 3.8,	N 10.6,	Cl 26.8%

EXAMPLE XVIII.
Preparation of 2-(2,6-dichlorophenyl)benzimidazole



A solution of 2,6-dichlorobenzaldehyde (5.8 w) and *o*-phenylenediamine (3.6 w) in methanol (50 v) was added to a solution of cupric acetate (6.5 w) in aqueous methanol (100 v) at 70°C. The mixture was heated in a boiling water bath for one hour, then filtered and the solid washed well with dilute sulphuric acid and hot water. Suffi-

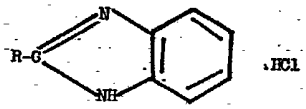
cient ammonium hydroxide was added to the filtrate to form a solution of cuprammonium salt and to precipitate the benzimidazole derivative. The latter was filtered off and crystallised from a mixture of ethanol and light petroleum. The product had m.p. 278° to 280°C.

Analysis

Found: C 59.7, H 3.1, N 10.9, Cl 27.3%
$C_{13}H_8Cl_2N_2$ requires: C 59.3, H 3.0, N 10.6, Cl 27.0%

EXAMPLE XIX.

Preparation of 2-(2,6-dichlorophenyl)benzimidazole hydrochloride



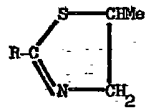
To a solution of 2,6-dichlorobenzaldehyde (5.8 w) and o-phenylenediamine (3.6 w) heated on a water bath was added gradually a solution of cupric acetate (6.5 w) in aqueous methanol (15.0 v). The yellow solid formed was filtered off, heated with dilute hydrochloric acid and then crystallised from methanol. The product had m.p. above 360°C.

Analysis

Found: C 52.0, H 3.3, N 9.5, Cl 33.9, Cl⁻ 11.8%
$C_{13}H_9Cl_3N_2$ requires: C 52.0, H 3.0, N 9.3, Cl 35.5, Cl⁻ 11.8%

EXAMPLE XX.

Preparation of 2-(2,6-dichlorophenyl)-5-methyl-2-thiazoline



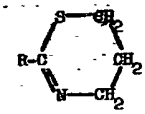
A mixture of N-(2-hydroxypropyl)-2,6-dichlorobenzamide (7.0 w) and phosphorus pentasulphide (5.0 w) in toluene (100 v) was refluxed for 12 hours. The toluene layer was decanted and extracted with dilute aqueous hydrochloric acid and the gummy residue extracted with hot dilute hydrochloric acid. The acid extracts were combined and then made alkaline. The product was extracted with chloroform, the extract dried over anhydrous magnesium sulphate, the chloroform removed and the residue distilled. The portion boiling at 187° to 188°C. under 12 mm pressure was collected. Yield 2.0 w.

Analysis

Found: C 48.6, H 3.6, N 5.9, Cl 29.9, S 13.4%
$C_{10}H_9Cl_2NS$ requires: C 48.8, H 3.7, N 5.7, Cl 28.9, S 13.0%

EXAMPLE XXI.

Preparation of 2-(2,6-dichlorophenyl-5:6-dihydro-4H-1,3-thiazine



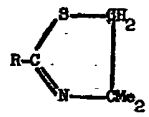
A mixture of N-(3¹-hydroxy-propyl)-2,6-dichlorobenzamide (10 w) and phosphorus pentasulphide (5 w) in toluene (100 v) was refluxed for 12 hours. The toluene layer was then decanted and the gummy residue extracted with hot dilute aqueous hydrochloric acid. The acid extract was then made alkaline and the precipitated solid was filtered off, washed with water, dried and recrystallised from light petroleum (b.p. 80°—100°C.). A further quantity of product was obtained by extracting the toluene layer with aqueous hydrochloric acid, working up the extract in the same way. Total yield of recrystallised product 4 w, m.p. 103° to 104°C.

Analysis

Found: C 48.9, H 3.4, N 5.9, Cl 29.0, S 13.1%
$C_{10}H_9Cl_2NS$ requires: C 48.8, H 3.7, N 5.7, Cl 28.9, S 13.0%

EXAMPLE XXII.

Preparation of 2-(2,6-dichlorophenyl)-4,4-dimethyl-2-thiazoline



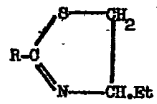
This compound was prepared from N-(2-hydroxy-1,1-dimethylethyl)-2,6-dichlorobenzamide R . CO . NH . CMe_2 . CH_2OH (7.0 w) and phosphorus pentasulphide (5.0 w) by the method described in Example XXII. The product (4.5 w) had m.p. 45° to 47°C. and b.p. 183°C. to 184°C. under 20 mm. pressure.

Analysis

Found: C 50.9, H 4.3, N 5.8, Cl 27.4, S 12.7%
$C_{11}H_{11}Cl_2NH$ requires: C 50.8, H 4.2, N 5.4, Cl 27.3, S 12.3%

EXAMPLE XXIII.

Preparation of 2-(2,6-dichlorophenyl)-4-ethyl-2-thiazoline



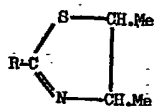
This compound was prepared from N-(2-hydroxy-1-ethylethyl)-2,6-dichlorobenzamide R . CO . NH . CHEt . CH_2OH (7.0 w) and phosphorus pentasulphide (5.0 w) by the method described in Example XXII. The product had b.p. 206°C. under 20 mm pressure. Yield 3 w.

Analysis

Found: C 50.9, H 4.3, N 5.6, Cl 28.3, S 13.5%
$C_{11}H_{11}Cl_2NS$ requires: C 50.8, H 4.2, N 5.4, Cl 27.3, S 12.3%

EXAMPLE XXIV.

Preparation of 2-(2,6-dichlorophenyl)-4,5-dimethyl-2-thiazoline



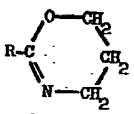
This compound was prepared from N-(2-hydroxy-1,2-dimethylethyl)-2,6-dichlorobenzamide R . CO . NH . CHMe . CHMeOH (7.0 w) and phosphorus pentasulphide (5.0 w) by the method described in Example XXII. The product had b.p. 193°—194°C. under 12 mm. pressure. Yield 4 w.

Analysis

Found: C 51.0, H 4.4, N 5.8, Cl 28.0, S 11.8%
$C_{11}H_{11}Cl_2NS$ requires: C 50.8, H 4.2, N 5.4, Cl 27.3, S 12.3%

EXAMPLE XXV.

Preparation of 2-(2,6-dichlorophenyl)-5,6-dihydro-4H-1,3-oxazine



N-(3-hydroxypropyl)-2,6-dichlorobenzamide (5.0 w) was heated in polyphosphoric acid (15.0 v) at 160°C. for 5 hours. The mixture was poured into water, made alkaline with potassium carbonate and extracted with chloroform. The extract was dried over magnesium sulphate, the solvent removed and the residue left to crystal-

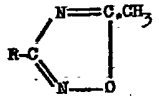
lise. It was then dissolved in light petroleum (b.p. 80° to 100°C.), the solution treated with carbon, the solvent removed and the residue left to crystallise. It had m.p. 43° to 45°C. Yield 3 w.

Analysis

Found: C 51.9, H 4.0, N 6.4, Cl 30.9%
$C_{10}H_5Cl_2NO$ requires: C 52.0, H 3.9, N 6.1, Cl 30.9%

EXAMPLE XXVI.

Preparation of 3-(2,6-dichlorophenyl)-5-methyl-1,2,4-oxadiazole



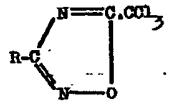
2,6-Dichlorobenzamidoxime (10.25 w) dissolved in glacial acetic acid was treated with acetic anhydride (6 w). The reaction mixture was then poured into water and the O-acetyl-α-amino-2,6-dichlorobenzaldoxime recovered in almost quantitative yield. The O-acetyl derivative was heated at 170°C. until water was no longer evolved. The residue was recrystallised from benzene and was then obtained in almost quantitative yield. It had m.p. 82° to 84°C.

Analysis

Found: C 47.2, H 2.8, Cl 31.6%
$C_9H_6Cl_2N_2O$ requires: C 47.2, H 2.6, Cl 31.0%

EXAMPLE XXVII.

Preparation of 3-(2,6-dichlorophenyl)-5-trichloromethyl-1,2,4-oxadiazole



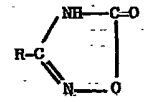
O-Trichloroacetyl-α-amino-2:6-dichlorobenzaldoxime was heated at 170°C. until water was no longer evolved. The residue was recrystallised from benzene and was then obtained in almost theoretical yield. It had m.p. 93°C.

Analysis

Found: C 32.7, H 0.7, Cl 53.5%
$C_9H_3Cl_5N_2O$ requires: C 32.5, H 0.9, Cl 53.4%

EXAMPLE XXVIII.

Preparation of 3-(2,6-dichlorophenyl)-1,2,4-oxadiazol-2-in-5-one



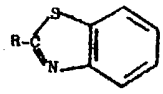
O-Ethoxycarbonyl-α-amino-2,6-dichlorobenzaldoxime $R.C(NH_2):NO.COOEt$, obtained by reacting 2,6-dichloro-α-aminobenzaldoxime with an equivalent amount of ethyl chloroformate and triethylamine in ethereal solution, was heated at 170°C. for 15 minutes. The ethanol produced was collected and found to be practically theoretical in amount. The residue was recrystallised from a mixture of ether and light petroleum (b.p. 40—60°C.) and was obtained in the form of colourless crystals, m.p. 173°C.

Analysis

Found: N 11.9 Cl 30.0%
$C_8H_4Cl_2N_2O_2$ requires: N 12.1 Cl 30.7%

EXAMPLE XXIX.

Preparation of 2-(2,6-dichlorophenyl) benzothiazole



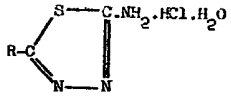
N-Phenyl-2,6-dichlorothiobenzamide (4.0 w) in ethanol (60 v) was added gradually to a mixture of potassium ferricyanide (38.6 w), sodium hydroxide (3.5 w) and water (100 v) at 90° to 100°C. The resulting mixture was heated at 90° to 100°C. for a further two hours, then filtered and the product crystallised from light petroleum (b.p. 60° to 80°C.). It then had m.p. 95°C. Yield 1.0 w.

Analysis

Found:	C 56.1;	H 2.6,	N 4.9,	Cl 25.3,	S 12.0%;
$C_{13}H_7Cl_2NS$ requires:	C 55.7	H 2.5,	N 5.0,	Cl 25.4,	S 11.4%;

EXAMPLE XXX.

Preparation of 2-(2,6-dichlorophenyl)-5-amino-1,3,4-thiadiazole hydrochloride hydrate



2,6-Dichlorobenzylidene thiosemicarbazone (12.4 w), ferric chloride (9.0 w) and water (200 v) were heated together at 90° to 100°C. for four hours, then filtered and the filtrate cooled. A solid crystallised, m.p. 213° to 215°C. Yield 1.0 w.

Analysis

Found:	C 31.5,	H 2.5,	Cl 35.9,	S 10.5,	Cl^- 11.4%
$C_8H_8Cl_3N_3OS$ requires:	C 32.0,	H 2.7,	Cl 35.5,	S 10.7,	Cl^- 11.8%;

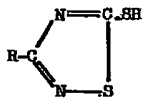
The free base was prepared by treating an aqueous solution of the hydrochloride with concentrated ammonium hydroxide. The resulting precipitate was filtered off and crystallised from a mixture of chloroform and light petroleum. It had m.p. 257° to 259°C.

Analysis

Found:	C 38.7,	H 2.3,	Cl 27.9,	S 13.3%;	
$C_8H_5Cl_2N_3S$ requires:	C 39.0,	H 2.0,	Cl 28.8,	S 13.0%;	

EXAMPLE XXXI.

Preparation of 3-(2,6-dichlorophenyl)-5-mercapto-1,2,4-thiadiazole



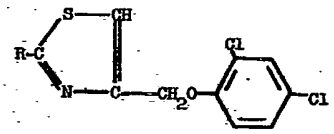
2,6-Dichlorobenzamidoxime (205 w; 1 mol.) was dissolved in methanol (100 v) and carbon disulphide (760 w; 10 mol.) was added followed by an amount of distilled water just sufficient to cause separation into two layers. The mixture was gently heated under reflux for 3 hours and then allowed to stand for 2 days. The solvents were then removed under reduced pressure and the residue treated with concentrated hydrochloric acid (200 v) which caused vigorous gas evolution. Distilled water (1000 v) was added, the mixture heated to boiling and the acid solution removed. The desired mercaptan was extracted from the residue by dissolving it in aqueous sodium hydroxide and re-acidifying the solution. On recrystallisation from benzene it was obtained in shining plates, m.p. 150°C.

Analysis

Found:	C 36.1,	H 1.6,	N 10.9,	Cl 26.2,	S 24.4%;
$C_8H_4Cl_2N_2S_2$ requires:	C 36.5,	H 1.5,	N 10.6,	Cl 27.0,	S 24.4%;

EXAMPLE XXXII.

Preparation of 4-(2,4-dichlorophenoxymethyl)-2-(2,6-dichlorophenyl)-1,3-thiazole



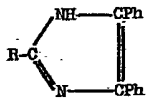
The product of Example VII (5 w) in methanol (25 v) was added to a solution from 2,4-dichlorophenol (3.2 w) and potassium hydroxide (1.2 w) in methanol (200 v) and the mixture refluxed for 6 hours. The methanol was then distilled off and the residue extracted 4 times with ether (50 v). The combined ether extracts were washed with 2N-sodium hydroxide solution, then with water and dried over anhydrous magnesium sulphate. The ether was then distilled off and the residue crystallised from light petroleum (b.p. 60° to 80°C.) when it was obtained as flat needles (2.5 w) m.p. 85°C.

Analysis

Found:	C 47.3,	H 2.0,	N 3.6,	Cl 34.4,	S 7.9%
$C_{16}H_9Cl_4NOS$ requires:	C 47.5,	H 2.2,	N 3.5,	Cl 35.0,	S 7.9%

EXAMPLE XXXIII.

Preparation of 2-(2,6-dichlorophenyl)-4,5-diphenylimidazole

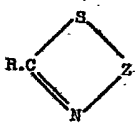


A mixture of benzil (5.25 w), 2,6-dichlorobenzaldehyde (4.1 w) and ammonium acetate (150 w) in glacial acetic acid (125 v) was refluxed for one hour. The reaction mixture was then cooled, poured into water and the solid filtered off and crystallised from ethanol. The product had m.p. 241° to 242°C.

Analysis

Found:	N 7.6,	Cl 19.6%		
$C_{21}H_{14}Cl_2N_2$ requires:	N 7.6,	Cl 19.5%		

The compounds of the invention possess, *inter alia*, herbicidal activity. Particularly high herbicidal activity is exhibited by those compounds having the general formula



wherein Z represents an alkylene group of 2 to 4 carbon atoms, preferably of 2 carbon atoms, which may be unsubstituted, or substituted by at least one alkyl group of 1 to 4 carbon atoms, preferably methyl or ethyl.

These preferred compounds are highly toxic to germinating seeds and are therefore suitable for use in destroying weed seeds in areas prior to sowing or planting a crop. Some compounds are toxic when sprayed on foliage. The results of pre-emergence herbicidal tests carried out with some of the more active compounds of the invention are summarised in the following Table. These tests were carried out as follows:—

Aqueous compositions containing acetone (40 v), water (60 v), Triton X 155 (0.5% w/v) and the compound specified in logarithmically varying concentrations were used. Soil spray tests were carried out in which seeds (oat (O), ryegrass (RG), sweet corn (SC), pea (P), sugar beet (SB), linseed (L) and mustard (M) were sown in sterile No. 1 John Innes compost and sprayed at 50 gallons per acre. Control tests in which seeds were similarly sprayed with the aqueous acetone—Triton X 155 solution only

were also carried out. The phytotoxic effect of the compound applied was assessed by determining the reduction from the control in fresh weight of stem and leaf of the test plants and a regression curve relating growth inhibition and dosage period. The dosage of the compound required for 90% growth inhibition is given in the Table. Dosages greater than 10 pounds per acre are indicated by X. "Triton" is a Trade Mark.

TABLE

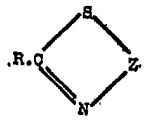
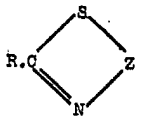
 Compound wherein R represents a 2,6-phenyl dichloro group. Z=		Growth inhibition dose (lb/ac) when compound applied as pre-emergence soil spray						
		O	RG	SC	P	SB	L	M
—$CH_2.CH_2$—		<0.9	7.2	X	5.9	6.6	X	X
—$CH_2.CH_2$—	.HBr	<0.9	<0.9	1.4	1.7	<0.9	0.9	1.0
—$CH_2.CH_2.CH_2$—		3.5	<0.9	9.3	6.7	2.3	X	X
—$CH_2.CH_2.CH_2$—	.HBr	<0.9	<0.9	1.9	3.7	<0.9	1.4	1.3
—$CH_2.CH_2.CH_2$—	.HCl	2.2	<0.9	6.8	8.3	1.9	6.0	6.0
—$CH_2.CH_2.CH_2.CH_2$—		<1.2	<1.2	X	5.7	1.3	2.0	5.8
—$CH_2.CH_2.CH_2.CH_2$—	.HBr	1.6	<1.2	X	X	2.8	X	X
—CHMe.CH_2—		3.7	4.0	X	8.5	6.7	X	X
—CH_2.CHMe—		4.4	3.7	X	9.3	7.2	X	X
—CH_2.CHMe—	.HCl	4.0	4.6	X	9.3	9.0	X	X

TABLE (*Continued*)

 Compound wherein R represents a 2,6-phenyl dichloro group. Z=	Growth inhibition dose (lb/ac) when compound applied as pre-emergence soil spray						
	O	RG	SC	P	SB	L	M
—CH_2.CHEt—	4.1	6.1	X	X	X	X	X
—CHMe.CHMe—	7.2	8.0	X	X	X	X	X
—CH=CHMe— .HCl	3.6	5.2	X	5.8	5.2	X	9.7
—CH_2.CO—	<0.9	<0.9	2.5	2.5	<0.9	<0.9	1.4
—CHMe.CO—	<0.9	<0.9	4.7	2.9	<0.9	1.9	2.5
—CHEt.CO—	1.4	<0.9	7.5	5.5	1.1	3.6	4.2
—CHPr^n.CO—	<1.2	<1.2	7.5	4.4	<1.2	<1.2	1.9
—CHBu^n.CO—	<1.2	<1.2	2.0	1.8	<1.2	<1.2	<1.2
—CHCOOEt.CO—	2.3	1.6	X	X	1.5	4.5	5.5

Some of the novel compounds of the invention, e.g. 4-methyl-2-(2,6-dichlorophenyl)-1,3-thiazole hydrochloride, 4-chloromethyl-2-(2,6-dichlorophenyl)-1,3-thiazole, 2-(2,6-dichlorophenyl)-2,3-dihydrobenzoxazole, and 3-(2,6-dichlorophenyl)-5-mercapto-1,2,4-thiadiazole, also exhibit fungicidal activity when tested in spore germination tests carried out with spores of *Alternaria brassiccicola* on wall flower leaves and/or when tested against *Aspergillus niger* on agar. Some compounds are toxic to *Pseudomonas putrefaciens* (*P.p.*) and to *Bacillus subtilis* (*B.s.*) in peptone broth cultures. For example 4-methyl-2-(2,6-dichlorophenyl)-1,3-thiazole hydrochloride, 2-(2,6-dichlorophenyl)-2,3-dihydrobenzoxazole and 3-(2,6-dichlorophenyl)-5-mercapto-1,2,4-thiadiazole are toxic to *B.s.* and the last two mentioned compounds are toxic to *P.p.*

This invention relates further to compositions comprising a compound as hereinbefore specified as active ingredient and a carrier or a surface active agent, or a carrier and a surface active agent.

The term "carrier" as used herein means a material, which may be inorganic or organic and synthetic or of natural origin, with which the active substance is mixed or formulated to facilitate its storage, transport and handling and its application to the plant, seed, soil or other object to be treated. The carrier is preferably biologically and chemically inert. It may be a solid or a fluid. Solid carriers are preferably particulate, granular or pelleted though other shapes and sizes are not thereby excluded. Solid carriers generally obtainable in particulate, granular or pelleted form, may be naturally occurring minerals, for example a clay, though they have have been subjected to grinding, sieving, purification and other treatments. Carriers produced synthetically, for example, synthetic hydrated silicon oxides and synthetic calcium silicates may also be used and many proprietary products of this type are available commercially. The product available as Silicium dioxyd No 3 is a particularly suitable carrier of this type. The carrier may also be an elemental substance such as sulphur or carbon, preferably an activated carbon. If the carrier possesses intrinsic catalytic activity such that it would decompose the active ingredient it is advantageous to incorporate a stabilising agent.

For some purposes, a resinous or waxy carrier may be used, preferably one which is solvent soluble or thermoplastic, including fusible. Examples of such carriers are natural or synthetic resins such as a coumarone resin, rosin, copal, shellac, dammar, polyvinyl chloride, styrene polymers and copolymers, a solid grade of polychlorophenol such as is available under the Registered Trademark "Aroclor", a bitumen, an asphaltite, a wax, for example beeswax or a mineral wax such as paraffin wax or Montan wax, or a chlorinated mineral wax. Compositions comprising such resinous or waxy carriers are preferably in granular or pelleted form.

Fluid carriers may be liquids, for example an aqueous fluid, or an organic fluid, including a liquefied normally vaporous or gaseous material, or a vaporous or gaseous material, and may be solvents or non-solvents for the active ingredient. Suitable solvents include petroleum fractions boiling in the kerosine and gas oil ranges and aromatic extracts thereof, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, aromatic hydrocarbons, such as benzene, toluene, and chlorinated hydrocarbons, for example carbon tetrachloride and the dichlorbenzenes.

The carrier may also be a simple or compound fertiliser which may be a solid, preferably granular or pelleted, or a liquid, for example an aqueous solution.

The carrier may be mixed or formulated with the active material during its manufacture or at any stage subsequently. The carrier may be mixed or formulated with the active material in any proportion. One or more carriers may be used.

The compositions of the invention may be concentrates, suitable for storage or transport and containing, for example, from 10 to 95% by weight of the active ingredient. These can be diluted with the same or a different carrier to a concentration suitable for application. The compositions of the invention may also be dilute compositions suitable for application. In general, concentrations of 0.01 to 0.5% by weight of active ingredient, based on the total weight of the composition, are satisfactory, though lower and higher concentrations can be applied if necessary. Effective weed control is obtainable by applying the compositions at the rate of 1 to 20 pounds per acre of the active ingredient.

The compositions of the invention may be formulated as dusts. These comprise an intimate mixture of the active ingredient and a finely powdered solid carrier such as is indicated above. These powder carriers may be oil-treated to improve adhesion to the surface to which they are applied. These dusts may be concentrates, in which case a highly sorptive carrier is preferably used. These require to be diluted with the

same or a different finely powdered carrier, which may be of lower sorptive capacity, to a concentration suitable for application.

The compositions of the invention may be formulated as wettable powders comprising a major proportion of the active ingredient mixed with a dispersing, i.e. deflocculating or suspending, agent and, if desired, a finely divided solid carrier. The active ingredient may be in particulate form or adsorbed on the carrier and preferably constitutes at least 10%, more preferably at least 50% by weight of the composition. The concentration of the dispersing agent should in general be between 0.1 and 10% by weight of the total composition though larger or smaller amounts may be used if desired.

The dispersing agent used in the composition of the invention may be any substance having definite dispersing, i.e. deflocculating or suspending properties as distinct from wetting properties, although these substances may also possess wetting properties.

The dispersing agent used may be a protective colloid such as gelatin, glue, casein, gums or a synthetic polymeric material such as polyvinyl alcohol. Preferably, however, the dispersing agents used are sodium or calcium salts of high molecular weight sulphonic acids, e.g. the sodium or calcium salts of lignin sulphonic acids derived from sulphite cellulose waste liquors. The calcium or sodium salts of condensed aryl sulphonic acids and sodium salts of polyacrylic acids are also suitable.

The dispersing agents used may be non-ionic or ionic, for example the condensation products of fatty acids containing at least 12, preferably 16 to 20, carbon atoms in the molecule with alkylene oxides such as ethylene oxide or propylene oxide or with both ethylene oxide and propylene oxide; partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol or mannitol, or condensation products of alkyl phenols, e.g. *p*-octyl cresol with the above alkylene oxides or their sulphated or sulphonated derivatives.

The dispersing agents referred to above may also possess wetting properties but in general it is preferable to incorporate two separate surface active agents, one having particularly good dispersing properties and the other having particularly good wetting properties. The actual amount of wetting agent incorporated can be varied considerably and in general is from 0 to 10% by weight based on the total composition.

Suitable wetting agents include the alkali metal salts, preferably sodium salts, of sulphuric acid esters or sulphonic acids containing at least 10 carbon atoms in the molecule. Non-ionic wetting agents may also be employed, for example polyalkylene oxide polymers, e.g. the "Pluronics" (Trade Mark), and the above mentioned condensation products of alkyl phenols with alkylene oxides.

Granulated or pelleted compositions comprising a suitable carrier and the active ingredient incorporated therewith are also included in the invention. These may be prepared by impregnating a granular carrier with a solution of the active ingredient or by granulating a mixture of a finely divided solid carrier and the active ingredient. The carrier used may consist of or contain a fertiliser or fertiliser mixture, for example superphosphate.

The compositions of the invention may also be formulated as solutions of active ingredient in an organic solvent or mixture of solvents. Suitable solvents include alcohols, ketones, especially acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, ethers, aromatic hydrocarbons, chlorinated hydrocarbons, petroleum hydrocarbon fractions and aromatic extracts of kerosine. Auxiliary solvents such as alcohols, ketones and polyalkylene glycol ethers and esters may be used in conjunction with these petroleum solvents. Such oil solutions are particularly suitable for application by low volume spraying for example at the rate of 5 to 10 gallons per acre. They may also be diluted with a cheap solvent for high volume spraying.

Compositions of the present invention may also be formulated as emulsifiable concentrates which are concentrated solutions or dispersions of the active ingredient in an organic liquid, preferably a water-insoluble organic liquid, containing an added emulsifying agent. These concentrates may also contain a proportion of water for example up to 50% by volume, based on the total composition (i.e. a "mayonnaise" composition) to facilitate subsequent dilution with water. Suitable organic liquids are for example the above mentioned petroleum hydrocarbon fractions.

The emulsifying agent may be of the type producing water-in-oil or oil-in-water type emulsions which are suitable for application by low volume spraying, or an emulsifier of the type producing oil-in-water emulsions producing concentrates which can be diluted with relatively large volumes of water for application by high volume spraying may be used.

Suitable types of emulsifier for use in these emulsions or emulsifiable concen-

trates are the non-ionic and anionic dispersing and wetting agents described above, also suitable are long chain alkyl ammonium salts and alkyl sulpho-succinates.

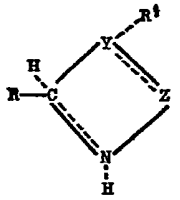
The concentration of emulsifier used will in general be within the limits 0.5% and 25.0% based on the final composition.

The compositions of the invention may contain other ingredients, for example, water conditioning agents for example, sodium polyphosphates, cellulose ethers, or ethylene diamine tetra-acetic acid, other herbicides or pesticides, or stickers, for example a non-volatile oil.

Aqueous dispersions and emulsions, for example, compositions obtained by diluting the wettable powders or emulsifiable concentrates of the present invention with water also lie within the scope of the present invention.

WHAT WE CLAIM IS:—

1. Compounds of the general formula:



wherein the carbon and nitrogen atoms are linked either by a double bond or by a single bond and the remaining valencies of said atoms attached to hydrogen atoms;

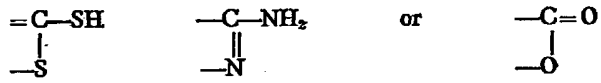
R represents a 2,6-dihalophenyl group;

Y represents an oxygen, sulphur or nitrogen atom, the third valency of said nitrogen atom being attached either to Z to form a double bond therewith; or to R^1, R^1 representing a hydrogen atom or a phenyl group;

Z represents an organic group which with the atoms to which it is linked, completes a heterocyclic ring; and the acid addition salts thereof.

2. Compounds as claimed in claim 1 wherein R represents a 2,6-dichlorophenyl group.

3. Compounds as claimed in claim 1 or 2 wherein Z represents an alkylene, alkeneoxy, alkylenecarbonyl or alkenylene group containing up to 4 carbon atoms which group may contain alkyl, haloalkyl, chlorophenoxyalkyl, phenyl, halophenyl or alkoxycarbonyl substituents, or a phenylene or tetrahydrophenylene group, or one of the following groups



4. Compounds as claimed in claim 3 wherein alkyl or haloalkyl substituents contain 1 to 4 carbon atoms.

5. Compounds as claimed in claims 3 or 4 wherein the haloalkyl or halophenyl substituents are chloro- or bromo-alkyl or chloro- or bromo-phenyl groups.

6. Acid addition salts of the compounds specified in any one of claims 1 to 5 which are salts of hydrochloric or hydrobromic acid.

7. 2-(2,6-Dichlorophenyl)-1,3-thiazoline.

8. 2-(2,6-Dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine and its hydrobromide.

9. 1-Phenyl-2-(2,6-dichlorophenyl)-1,4,5,6-tetrahydropyrimidine hydrobromide.

10. 2-(2,6-Dichlorophenyl)-4-methyl-1,3-thiazoline and its hydrochloride.

11. 3-(2,6-Dichlorophenyl)-4,5,6,7-tetrahydro-1,2,4-oxadiazepine hydrobromide.

12. 4-Methyl-2-(2,6-dichlorophenyl)-1,3-thiazole hydrochloride.

13. 4-Chloromethyl-2-(2,6-dichlorophenyl)-1,3-thiazole.

14. 2-(2,6-Dichlorophenyl)-4,5,6,7-tetrahydrobenzthiazole and its hydrochloride.

15. 4-(4-Bromophenyl)-2-(2,6-dichlorophenyl)-1,3-thiazole.

16. 2-(2,6-Dichlorophenyl)-1,3-thiazol-2-in-4-one.

17. 5-Ethyl-2-(2,6-dichlorophenyl)-1,3-thiazolin-4-one.

18. 2-(2,6-Dichlorophenyl)-5-*n*-propyl-1,3-thiazol-2-in-4-one.

19. 5-*n*-Butyl-2-(2,6-dichlorophenyl)-1,3-thiazol-2-in-4-one.
20. 2-(2,6-Dichlorophenyl)-5-ethoxycarbonyl-1,3-thiazolin-4-one.
21. 2-(2,6-Dichlorophenyl)-2,3-dihydrobenzoxazole.
22. 2-(2,6-Dichlorophenyl)-2,3-dihydrobenzothiazole.
23. 2-(2,6-Dichlorophenyl)benzimidazoline.
24. 2-(2,6-Dichlorophenyl)benzimidazole.
25. 2-(2,6-Dichlorophenyl)benzimidazole hydrochloride.
26. 2-(2,6-Dichlorophenyl)-5-methyl-2-thiazoline.
27. 2-(2,6-Dichlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine.
28. 2-(2,6-Dichlorophenyl)-4,4-dimethyl-2-thiazoline.
29. 2-(2,6-Dichlorophenyl)-4-ethyl-2-thiazoline.
30. 2-(2,6-Dichlorophenyl)-4,5-dimethyl-2-thiazoline.
31. 2-(2,6-Dichlorophenyl)-5,6-dihydro-4*H*-1,3-oxazine.
32. 3-(2,6-Dichlorophenyl)-5-methyl-1,2,4-oxadiazole.
33. 3-(2,6-Dichlorophenyl)-5-trichloromethyl-1,2,4-oxadiazole.
34. 3-(2,6-Dichlorophenyl)-1,2,4-oxadiazol-2-in-5-one.
35. 2-(2,6-Dichlorophenyl)benzothiazole.
36. 2-(2,6-Dichlorophenyl)-5-amino-1,3,4-thiadiazole hydrochloride hydrate.
37. 3-(2,6-Dichlorophenyl)-5-mercapto-1,2,4-thiadiazole.
38. 4-(2,4-Dichlorophenoxymethyl)-2-(2,6-dichlorophenyl)-1,3-thiazole.
39. 2-(2,6-Dichlorophenyl)-4,5-diphenylimidazole.

40. Compositions comprising a compound claimed in any one of claims 1 to 39 together with a carrier or surface active agent, or a carrier and a surface active agent.

41. Compositions as claimed in claim 40 which are dusts, wettable powders, emulsifiable concentrates, or aqueous emulsions or dispersions.

42. Compositions as claimed in claim 40 or 41 substantially as hereinbefore described.

43. A method for eradicating weeds from areas to be used for growing crops which comprises applying to said areas a herbicidal compound claimed in any one of claims 1 to 39 or composition claimed in claims 40, 41 or 42.

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